97-526074/48 C02 (C07) DADI 98.03.27

BASF AG *WO 9735845-A1

96.03.27 96DE-1012032 (97.10.02) C07D 239/54, A01N 43/54, C07C 271/22, 275/24

New 1-methyl-3-benzyl-6-haloalkyl-uracil derivatives - useful as pre- or post-emergence, total or selective herbicides and as desiccants or defoliants, especially for cotton (Ger)

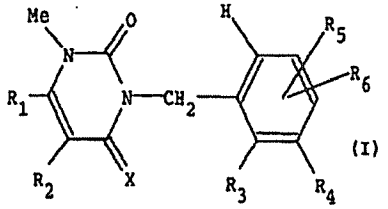
C97-167275 N(AU BG BR BY CA CN CZ GE HU IL JP KR KZ LV MX NO NZ PL RO RU SG SI SK TR UA US UZ VN) R(AT BE CH DE DK EA ES FI FR GB GR IE IT LU MC NL PT SE)

Addnl. Data: MENKE O, HAMPRECHT G, HEISTRACHER E, KLINTZ R, SCHAEFER P, ZAGAR C, MENGES M, WESTPHALEN K, WALTER H, MISSLITZ U

97.03.10 97WO-EP01203

C(7-D12, 14-U1A, 14-V1, 14-V2, 14-V3) .3

Substituted 1-methyl-3-benzyl-6-haloalkyl-uracil derivatives of formula (I) and their salts and enol ether derivatives are new.



(I)

reactant (IX)

X = O or S;

R_1 = 1-4C haloalkyl;

R_2 = H or halogen;

R_3 = H, CN, CNS, halogen, 1-4C haloalkyl, 1-4C haloalkoxy or 1-4C haloalkylthio;

R_4 = H, CN, CNS, halogen, 1-4C alkyl, 1-4C haloalkyl, 1-4C alkoxy, 1-4C haloalkoxy, 1-4C haloalkylthio or alkylaminocarbonyl;

R_5 = (i) H, CN, NO_2, OH, NH_2, halogen, 1-4C alkylamino (optionally

WO 9735845-A+

substituted by 1-4C alkyl, (1-4C)alkylcarboxyl (sic) or (1-4C)alkoxycarbonyl), haloalkoxy or haloalkylthio; or

(ii) alkoxy, alkylthio, cycloalkoxy, cycloalkylthio, alkenyloxy, alkenylthio, alkynyloxy, alkynylthio, alkylcarbonyloxy, alkylcarbonylthio, alkenylcarbonyloxy, alkenylcarbonylthio, alkynylcarbonyloxy, alkynylcarbonylthio, alkylsulphonyl or alkylsulphonyloxy (all optionally substituted by 1-3 of

(a) halogen, NO_2, CN, OH, cycloalkyl, alkoxy, cycloalkoxy, alkenyloxy, alkynyloxy, alkoxyalkoxy, alkylthio, alkylsulphinyl, alkylsulphonyl and 1-6C alkylideneamino;

(b) phenyl, phenoxy or phenylsulphonyl (all optionally substituted by 1-3 of halogen, NO_2, CN, alkyl, alkoxy and haloalkyl);

(c) 3-7 membered heterocyclyl or heterocyclyloxy (both optionally substituted by 1-3 of halogen, NO_2, CN, alkyl, alkoxy, haloalkyl and alkylcarbonyl); and

(d) COR_7, $COOR_7$, $COSR_7$, $CONR_7R_8$, $OCOR_7$, $OCOOR_7$, $OCOSR_7$, $OCONR_7R_8$ or NR_7R_8);

R_7 = H, alkyl, cycloalkyl, alkenyl, alkynyl, alkoxyalkyl, alkoxycarbonylalkyl, alkenyloxycarbonylalkyl, phenyl or phenylalkyl (where phenyl moieties are optionally substituted by 1-3 of halogen, NO_2, CN, alkyl, haloalkyl, alkoxy and alkylcarbonyl);

R_8 = H, OH, alkyl, cycloalkyl, alkoxy, alkoxycarbonylalkoxy, alkenyl or alkenyloxy; or

NR_7R_8 = 3-7 membered heterocycle (optionally substituted by 1-3 of halogen, NO_2, CN, alkyl, haloalkyl, alkoxy and alkylcarbonyl);

R_6 = (1) OH, SH, haloalkoxy or haloalkylthio;

(2) alkoxy, alkylthio, cycloalkoxy, cycloalkylthio, alkenyloxy, 5-7C cycloalkenyloxy, alkenylthio, alkynyloxy, alkynylthio, alkylcarbonyloxy, alkylcarbonylthio, alkoxycarbonyloxy, alkenylcarbonyloxy, alkenylcarbonylthio, alkynylcarbonyloxy, alkynylcarbonylthio, alkylsulphonyl or alkylsulphonyloxy [all optionally substituted by 1-4 groups selected from groups (a)-(d) given in R_5 (ii) (except that the Ph, PhO and $PhSO_2$ in (b) may additionally be substituted by alkoxycarbonyl), =O, =N-OR_{20}, -$C(R_{21})$=N-OR_{20} and $SiR_{30}R_{31}R_{32}$]; or

(3) -CYR_{11}, -$CR_{11}(Z_1R_{12})(Z_2R_{13})$, -$C(R_{11})$=$C(R_{14})$-Q, -$CHR_{11}CHR_{14}COR_{15}$, $COOR_{19}$, -C≡CCONHOR_{20}, -C≡CCON(R_{19})OR_{20}, -C≡CCSNHOR_{20}, -C≡CCSN(R_{19})OR_{20}, -C≡CC(R_{21})=NOR_{20}, -$NR_{23}R_{24}$ or -C≡C-Q';

R_{30}-R_{32} = alkyl or 2-6C alkenyl;

Z_1,Z_2 = O or S;

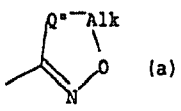
Q = CN, COR_{15}, CH_2COR_{15}, -$C(R_{16})$=$C(R_{17})COR_{15}$,

WO 9735845-A+/1

97-526074/48

$CH_2CHR_{18}COR_{15}$, $CONHOR_{20}$, CON(R_{19})OR_{20}, $CSNHOR_{20}$, CSN(R_{19})OR_{20}, $C(R_{21})$=NOR_{20} or Q';

Q' = heterocycle of formula (a);



(a)

Q" = O or S;

Alk = 1-3C alkylene (optionally substituted by alkyl);

R_{11} = H, CN, alkyl, haloalkyl, 2-6C alkenyl, 2-6C alkynyl, cycloalkyl, alkoxyalkyl or alkoxycarbonyl;

R_{12},R_{13} = alkyl, haloalkyl, alkenyl, alkynyl or alkoxyalkyl; or

R_{12}+R_{13} = 2-4 membered hydrocarbon chain which (i) is saturated or unsaturated, (ii) is optionally substituted by =O, (iii) optionally has one member (not adjacent to Z_1 or Z_2) replaced by O, S or N, (iv) is optionally substituted by 1-3 of CN, NO_2, NH_2, halogen, alkyl, 2-6C alkenyl, alkoxy, 2-6C alkenyloxy, 2-6C alkynyloxy, haloalkyl, cyanoalkyl, hydroxyalkyl, alkoxyalkyl,

alkenyloxyalkyl, alkynyloxyalkyl, cycloalkyl, cycloalkoxy, COOH, alkoxycarbonyl, alkylcarbonyloxyalkyl and phenyl (itself optionally substituted by 1-3 of CN, NO_2, NH_2, halogen, alkyl, haloalkyl, alkoxy and alkoxycarbonyl) and (v) optionally has 1 or 2 members forming part of a 3-7 membered ring (optionally containing 1 or 2 of O, S, N and N(alkyl) as heteroatom(s) and optionally substituted by 1 or 2 of CN, alkyl, 2-6C alkenyl, alkoxy, cyanoalkyl, haloalkyl and alkoxycarbonyl);

R_{14} = H, CN, halogen, alkyl, haloalkyl, alkoxy, alkylcarbonyl or alkoxycarbonyl;

R_{15} = H, OR_{22}, SR_{22}, alkyl (optionally mono- or disubstituted by alkoxy), 2-6C alkenyl, 2-6C alkynyl, haloalkyl, cycloalkyl, alkylthioalkyl, alkyliminooxy, $NR_{23}R_{24}$ or phenyl (optionally substituted by 1-3 of CN, NO_2, halogen, alkyl, 2-6C alkenyl, haloalkyl, alkoxy and alkoxycarbonyl);

R_{22} = as R_{19};

R_{23},R_{24} = H, alkyl, 2-6C alkenyl, 2-6C alkynyl, cycloalkyl, haloalkyl, alkoxyalkyl, alkylcarbonyl, alkoxycarbonyl, alkoxycarbonylalkyl, alkoxycarbonyl-(2-6C)alkenyl (optionally substituted in the

WO 9735845-A+/2

(con't)

alkenyl by 1-3 of halogen and CN), alkylsulphonyl, alkoxycarbonylalkylsulphonyl, phenyl or phenylsulphonyl (where phenyl moieties are optionally substituted by 1-3 of CN, NO_2, halogen, alkyl, alkenyl, haloalkyl, alkoxy and alkoxycarbonyl); or

$NR_{23}R_{24}$ = 4-7 membered saturated or unsaturated heterocycle, optionally containing a second O, S, -N=, NH or N(alkyl) heteroatom;

R_{16} = H, CN, halogen, alkyl, alkenyl, alkynyl, alkoxyalkyl, alkylcarbonyl, alkoxycarbonyl, $NR_{23}R_{24}$ or phenyl (optionally substituted by 1-3 of CN, NO_2, halogen, alkyl, alkenyl, haloalkyl, alkoxy and alkoxycarbonyl);

R_{17} = H, CN, halogen, alkyl, alkoxy, haloalkyl, alkylcarbonyl or alkoxycarbonyl;

R_{18} = H, CN, alkyl or alkoxycarbonyl;

R_{19} = (i) H; (ii) alkyl, haloalkyl, 2-6C alkenyl or 2-6C alkynyl (all optionally substituted by 1 or 2 of CN, halogen, OH, COOH, alkoxy, alkylthio, alkylcarbonyl, alkoxycarbonyl, alkylcarbonyloxy, alkenyloxycarbonyl and -CO-Het); (iii) alkylcarbonyl, haloalkylcarbonyl, alkoxycarbonyl, mono- or dialkylaminocarbonyl, alkoxyiminoalkyl or cycloalkyl; or (iii) phenyl or phenylalkyl (both optionally ring-substituted by 1-3 of CN, NO_2, halogen, alkyl, haloalkyl, alkoxy and alkoxycarbonyl);

Het = N-bonded 3-7 membered aza-heterocycle optionally containing a second O or S heteroatom;

R_{20} = H, alkyl, haloalkyl, cycloalkyl, alkenyl, alkynyl, hydroxyalkyl, alkoxyalkyl, alkylthioalkyl, cyanoalkyl, alkylcarbonylalkyl, alkoxycarbonylalkyl, alkoxycarbonyl-(2-6C)alkenyl, alkylcarbonyloxyalkyl or phenylalkyl (optionally ring-substituted by 1-3 of CN, NO_2, halogen, alkyl, haloalkyl, alkoxy and alkoxycarbonyl);

R_{21} = (i) H or halogen; (ii) alkyl, haloalkyl, alkoxy, haloalkoxy, alkenyloxy, alkylthio, haloalkylthio, alkylcarbonyloxy, haloalkylcarbonyloxy, alkylsulphonyloxy or haloalkylsulphonyloxy (all optionally monosubstituted by OH, CN, COOH, alkoxy, alkylthio, alkylcarbonyl, alkoxycarbonyl, mono- or dialkylaminocarbonyl, or alkylcarbonyloxy); (iii)-CO-Het; (iv) alkylcarbonyl, haloalkylcarbonyl, alkoxycarbonyl, alkoxycarbonyloxy, alkylcarbonylthio, haloalkylcarbonylthio, alkoxycarbonylthio, 2-6C alkenyl, 2-6C alkenylthio, alkynyl, alkynyloxy, alkynylthio, (2-6C) alkynylcarbonyloxy, alkynylsulphonyloxy, cycloalkyl, cycloalkoxy, cycloalkylthio, cycloalkylcarbonyloxy or cycloalkylsulphonyloxy; or (v) phenyl, phenoxy, phenylthio, benzoyloxy, phenylsulphonyloxy,

phenylalkyl, phenylalkoxy, phenylalkylthio, phenylalkylcarbonyloxy or phenylalkylsulphonyloxy (all optionally ring-substituted by 1-3 of CN, NO_2, halogen, alkyl, haloalkyl, alkoxy and alkoxycarbonyl);

Y = O, S or $N(R_{27})$;

R_{27} = (i) H, OH, alkyl, alkenyl, alkynyl, cycloalkyl, haloalkyl, alkoxyalkyl, alkoxy, alkenyloxy, alkynyloxy, cycloalkoxy, 5-7C cycloalkenyloxy,. haloalkoxy, haloalkenyloxy, hydroxyalkoxy, cyanoalkoxy, cycloalkylalkoxy, alkoxyalkoxy, alkoxyalkenyloxy, alkylcarbonyloxy, haloalkylcarbonyloxy, alkylcarbamoyloxy, haloalkylcarbamoyloxy, alkylcarbonylalkyl, alkoxycarbonylalkyl, alkylcarbonylalkoxy, alkoxycarbonylalkoxy, alkylthioalkoxy or dialkylaminoalkoxy; (ii) phenyl, phenylalkoxy, phenylalkenyloxy or phenylalkynyloxy (all optionally ring-substituted by 1-3 of CN, NO_2, halogen, alkyl, haloalkyl, 2-6 alkenyl, alkoxy and alkoxycarbonyl; and with 1 or 2 CH_2 units of the aliphatic chains optionally replaced by O, S or N(alkyl)); (iii) heterocyclyl, heterocyclylalkoxy, heterocyclylalkenyloxy or heterocyclylalkynyloxy (all optionally ring-substituted by 1-3 of CN, NO_2, halogen, alkyl, haloalkyl, 2-6 alkenyl, alkoxy and alkoxycarbonyl; and with 1 or 2 CH_2 units of the aliphatic chains optionally replaced by O, S or N(alkyl)), where heterocycles are 3-7 membered; or (iv) $NR_{28}R_{29}$;

R_{28},R_{29} = H, alkyl, alkenyl, alkynyl, cycloalkyl, haloalkyl, alkoxyalkyl, alkylcarbonyl, alkoxycarbonyl, alkoxycarbonylalkyl, alkoxycarbonyl-(2-6C)alkenyl (optionally substituted in the alkenyl by 1-3 of halogen and CN) or phenyl (optionally substituted by 1-3 of CN, NO_2, halogen, alkyl, alkenyl, haloalkyl, alkoxy and alkoxycarbonyl); or

$NR_{28}R_{29}$ = 4-7 membered saturated or unsaturated heterocycle, optionally containing a further O, S, -N=, NH or N(alkyl) heteroatom;

if R_6 is in the 4-position (i.e. R_5 is in the 5-position), then :

R_6 may also = (4) $-CON(R_{19})OR_{20}$, $-C(R_{21})=NOR_{20}$, $-C(Z_1R_{12})(Z_2R_{13})OR_{22}$, $-C(Z_1R_{12})(Z_2R_{13})SR_{22}$, $-C(Z_1R_{12})(Z_2R_{13})NR_{23}R_{24}$, Q', $COOR_{22}$, $COSR_{22}$, $CONR_{23}R_{24}$, alkylthio alkylcarbonyl or alkyliminooxycarbonyl;

unless specified otherwise alkyl moieties have 1-6C and alkenyl, alkynyl and cycloalkyl moieties have 3-6C.

Enamine ester and enamine carboxylate intermediates of formulae (III) and (IV) (see 'Preparation') are also new.

USE

(I) are herbicides and plant desiccants/defoliants (all claimed). They are useful (i) as total herbicides or (at lower application rates) as selective herbicides for combatting grassy and other weeds in crops such as wheat, rice, maize, soya and cotton, (ii) as desiccants for drying the above-ground parts of crops such as potatoes, rape, sunflowers and soya to facilitate mechanical harvesting : (iii) for promoting abscission of fruit or (iv) for controlled defoliation of useful plants, especially cotton (claimed).

Application rate is 0.001-3.0 (preferably 0.01-1.0) kg/ha, pre- or post-emergence.

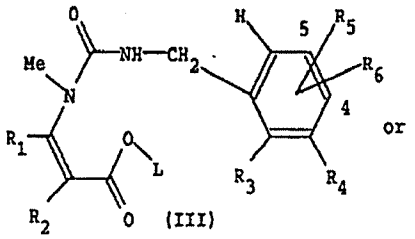
ADVANTAGE

(I) have stronger herbicidal activity against undesirable plants than related known compounds.

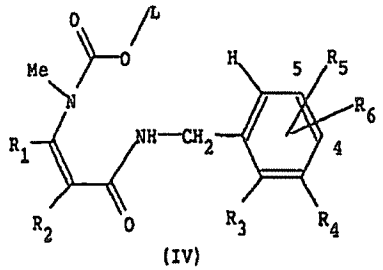
PREPARATION

The following processes are claimed.

(a)



(con't)

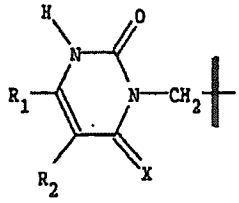


(IV)

cyclise, base → (I; X = O)

L = alkyl or phenyl.

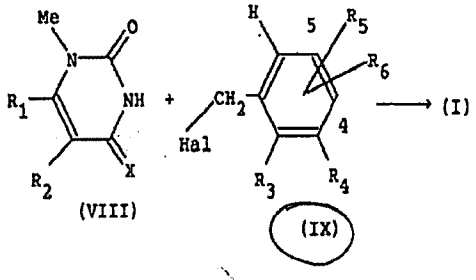
(b)



(V)

etc. → methylate → (I)

(c)



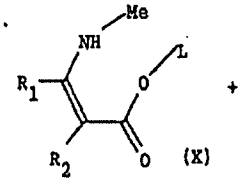
(VIII) + (IX) → (I)

Reaction is in presence of base, or (VIII) is used in alkali metal salt form.

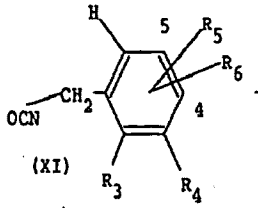
STARTING MATERIALS

(III) and (IV) are prepared e.g. as follows.

(a)

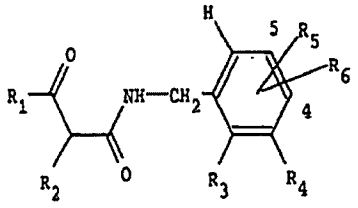


(X) +



(XI) → base → (III)

(b)



(XVII)

$CH_3NHCOOL$ → (IV)

EXAMPLE

A solution of 1.8g 3-(2,3-dichloro-4-isopropoxybenzyl)-2,4-dioxo-1H-6-trifluoromethyl-1,2,3,4-tetrahydropyrimidine in 50 ml DMF was treated with 0.7g K_2CO_3 and 0.7g MeI, stirred for 18 hrs. and treated with 150 ml ice-water. The solid product was isolated to give 1.4g of 3-(2,3-dichloro-4-isopropoxybenzyl)-2,4-dioxo-1-methyl-6-trifluoromethyl-1,2,3,4-tetrahydropyrimidine (Ia), m.pt. 167-168°C.

BIOLOGICAL ACTIVITY

(Ia) at 3.9 and 7.8 g/ha post-emergence showed good selective herbicidal activity against *Abutilon theophrasti*, *Amaranthus retroflexus* and *Solanum nigrum* in wheat. (RMH)

(117pp2400DwgNo.0/0)

SR:WO9504461